SYNTHESIS OF ENERGETIC MATERIALS
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Synthesis of Energetic Materials

Introduction

The work described in this report was carried out during 1982 under the sponsorship of the Office of Naval Research, Code 432 (Dr. R. S. Miller). The effort consisted of 2 separate tasks which will be discussed in turn: (1) synthesis of energetic monomers and polymers, and (2) synthesis of polycyclic and adamantoid nitramines. ~~Both tasks were continuations, and pre-1982 results were reported in ref.~~ 1. The principal objectives of the work are the synthesis of energetic (nitro) polymers with improved energy and physical properties, and the synthesis of nitramines with high crystal density and energy-density greater than HMX.

Energetic Monomers and Polymers

In continuation of the previous work under this task, the formation of hydroxy-terminated poly-formals from certain nitrodiols was investigated further. It had been shown[1] that 2,2,5,5-tetranitrohexanediol, 1, forms a linear formal with hydroxy termination on reaction with conc. H_2SO_4 and formaldehyde. This polymer was very attractive because of its high energy content and density. However, it had a rather high melting point and low solubility in energetic plasticizers as well as a higher than desired molecular weight. The molecular weight could not be modified by changing the reaction conditions.

In an effort to devise a more controllable polymer forming reaction, we have now prepared the bis(chloromethyl) ether of diol 1 as an intermediate for condensation with 1 in the presence of a Lewis acid catalyst.

$$\underset{\underline{1}}{HOCH_2C(NO_2)_2CH_2CH_2C(NO_2)_2CH_2OH} \xrightarrow[AlCl_3]{CH_2O} ClCH_2OCH_2C(NO_2)_2CH_2CH_2C(NO_2)_2CH_2OCH_2Cl$$

Yield ca. 70%

$$\xrightarrow{\underline{1}/\text{catalyst}} \text{Polyformal}$$

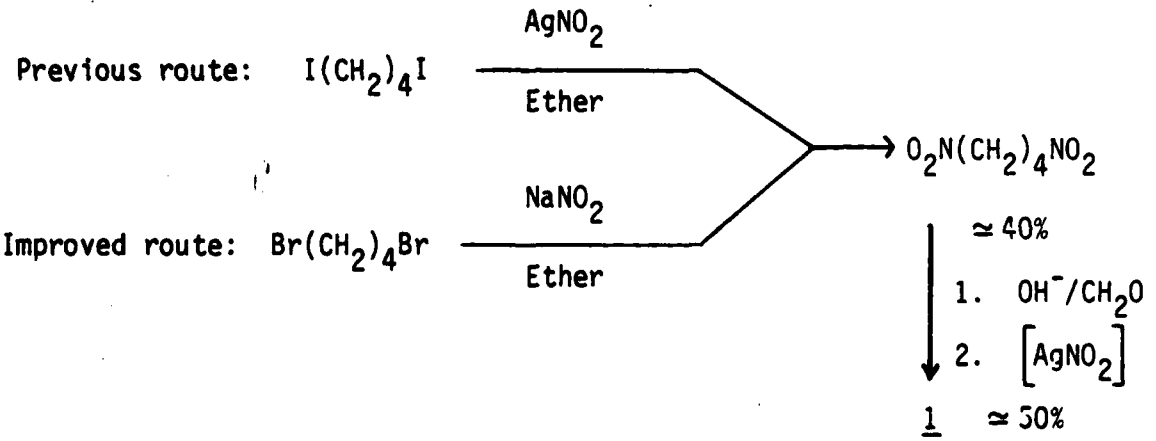
The second step has not been carried out since it was also found that polymers of varying and low molecular weight could be prepared directly by reaction of 1 and CH_2O in sulfolane with trifluoromethanesulfonic acid as catalyst. Interestingly enough, while the polymers prepared in concentrated sulfuric acid contained no

$$\underline{1} + CH_2O \xrightarrow[\text{sulfolane}]{CF_3SO_3H} \text{polyformal}$$

significant quantities of cyclic formals, those obtained with sulfolane/CF_3SO_3H contained both the 9- and 18-membered ring formals. A representative gel permeation chromatogram of the new material is shown in Fig. 1. This difference in the product composition is readily accounted for by the observation that in sulfolane the reaction mixture is homogeneous and the product is thus an equilibrium mixture of cyclic and linear formals, whereas in conc. sulfuric acid the linear polymer precipitates thus shifting the equilibrium in its favor.

The cyclic formals could be separated from the linear polymer by trituration with dichloromethane. In this fashion the polymer sample of mass maximun 1850 shown in Fig. 2 was prepared. Its melting point (120-130°C) was not significantly lower than those of the higher m.w. materials prepared earlier. This material was used for solubility measurements in nitroplasticizers. The solubility tests showed that the lower molecular weight polymer was somewhat more soluble than the material obtained last year, but was still not suitable for use with FEFO. The new polymer was soluble to the extent of approximately 20% at ambient temperature in dinitropropyl formal/acetal mixture (BDNPF/A) and this system may be suitable for use as a binder but would be of no great practical interest because of the low energy of BDNPF/A.

We conclude from the results obtained this year that the polyformal of 1 is not sufficiently soluble in currently available high energy plasticizers, and that a more polar plasticizer with energy comparable to FEFO (possibly a nitroester) would be needed to utilize it in energetic compositions. Polyacetals of 1 with acetaldehyde or nitrobutyraldehydes ($RC(NO_2)_2CH_2CH_2CHO$) might be more soluble in and compatible with FEFO, and the preparation of such acetals might be the subject of future work. Recently, Milt Frankel has improved the synthesis of 1 by the use of more readily available and cheaper materials in the first step[2] and further improvements are possible. 1 therefore remains of interest as a relatively readily accessible high energy nitrodiol.



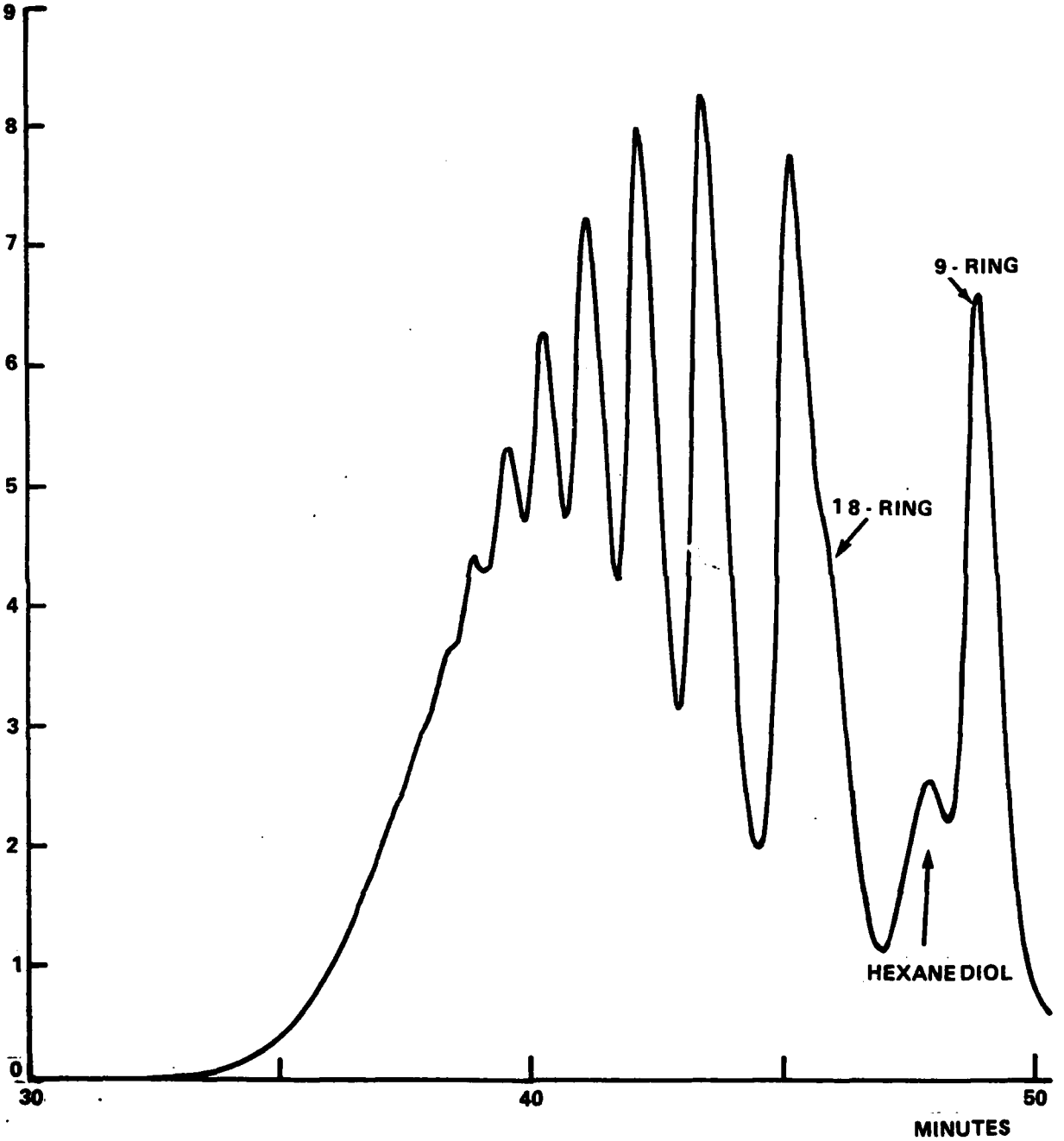


FIGURE 1. GP CHROMATOGRAM OF A POLYFORMAL OF 1 FROM SULFOLANE/CF_3SO_3H

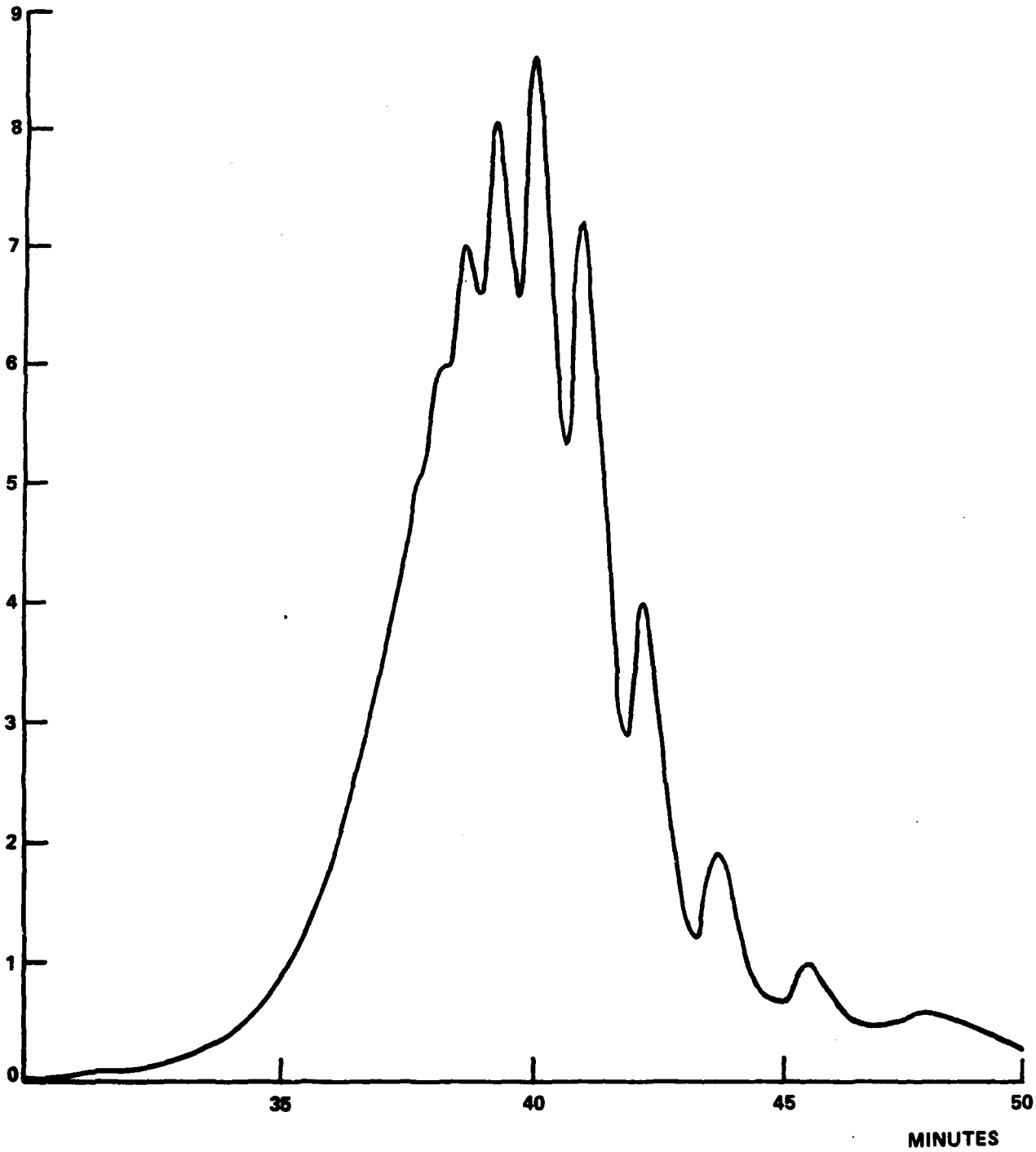


FIGURE 2. GP CHROMATOGRAM OF POLYFORMAL OF 1 AFTER SOLVENT TRITURATION

During the past year, we also investigated the preparation of polyformals from a second nitrodiol, 2, the synthesis of which is described in ref 1. This diol is about as energetic as 1, but has the advantage of having γ-nitrohydroxy groups;

$$HOCH_2CH_2C(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2C(NO_2)_2CH_2CH_2OH$$

2

this moiety is not subject to the reverse Henry reaction (deformylation) which apparently can lead to difficulties in the isocyanate curing of prepolymers with β-nitrohydroxy group termination[3].

Using 3,3-dinitrobutanol and 3,3,3-trinitropropanol as model substrates, it was found that formals of γ-nitroalcohols cannot be prepared by the method used for β-nitroalcohols (H_2SO_4/CH_2O), but are obtainable in good to excellent yields in acetonitrile and particularly sulfolane solvents with BF_3 etherate as catalyst.

$$RC(NO_2)_2CH_2CH_2OH \xrightarrow[\text{MeCN or sulfolane}]{\text{trioxane/}BF_3\text{ etherate}} \left[RC(NO_2)_2CH_2CH_2O\right]_2CH_2$$

R = NO_2: 60%

R = CH_3: 80-95%

When this reaction was applied to 2, mixtures of polymer and some cyclic formals were obtained. The molecular weights of the polymers and the ratio of polymer to cyclic formal depended on the solvent, on the amount of BF_3 etherate, and on the ratio of 2 to formaldehyde. The details of these relationships have not yet been worked out. Representative GPC curves of polymer obtained under different conditions are shown in figures 3 through 6. The highest molecular weight material (figure 6) prepared so far has a mass maximum in the GPC at about a molecular weight of 3200. The molecular weight of the polymer can be increased by the use of more formaldehyde; however this also increases the amount of cyclic formals because they too have a low ratio of 2: CH_2O (in fact they have the lowest ratio possible, i.e., 1).

The cyclic formals can be separated from the polymer by solvent extraction, for example with CH_2Cl_2/hexane mixtures, and can be recycled into the formal reaction because that reaction is carried out under equilibrium conditions, and any source of 2 and CH_2O will give the same end product, i.e., equilbrium mixture of polymer and cyclic formal.

We have carried out a preliminary characterization of the polymer corresponding to Fig. 5. The melting point is 50-85°C, and the melt is completely fluid at 85° but still somewhat turbid. Using the method of Baum (trimethylsilylation)[4], a functionality determination was carried out. This showed the polymer to be approximately difunctional although the analysis of the NMR was complicated by the presence of the cyclic formals and some silicon grease. The density of the polymer is about 1.55 g/cm^3; the heat of formation is estimated to be -326 cal/g, and the calculated detonation pressure is 211 Kbar (TNT, 206 Kbar). The polymer has good solubility in FEFO and excellent solubility in BDNPF/A, as the data in Table 1 indicate.

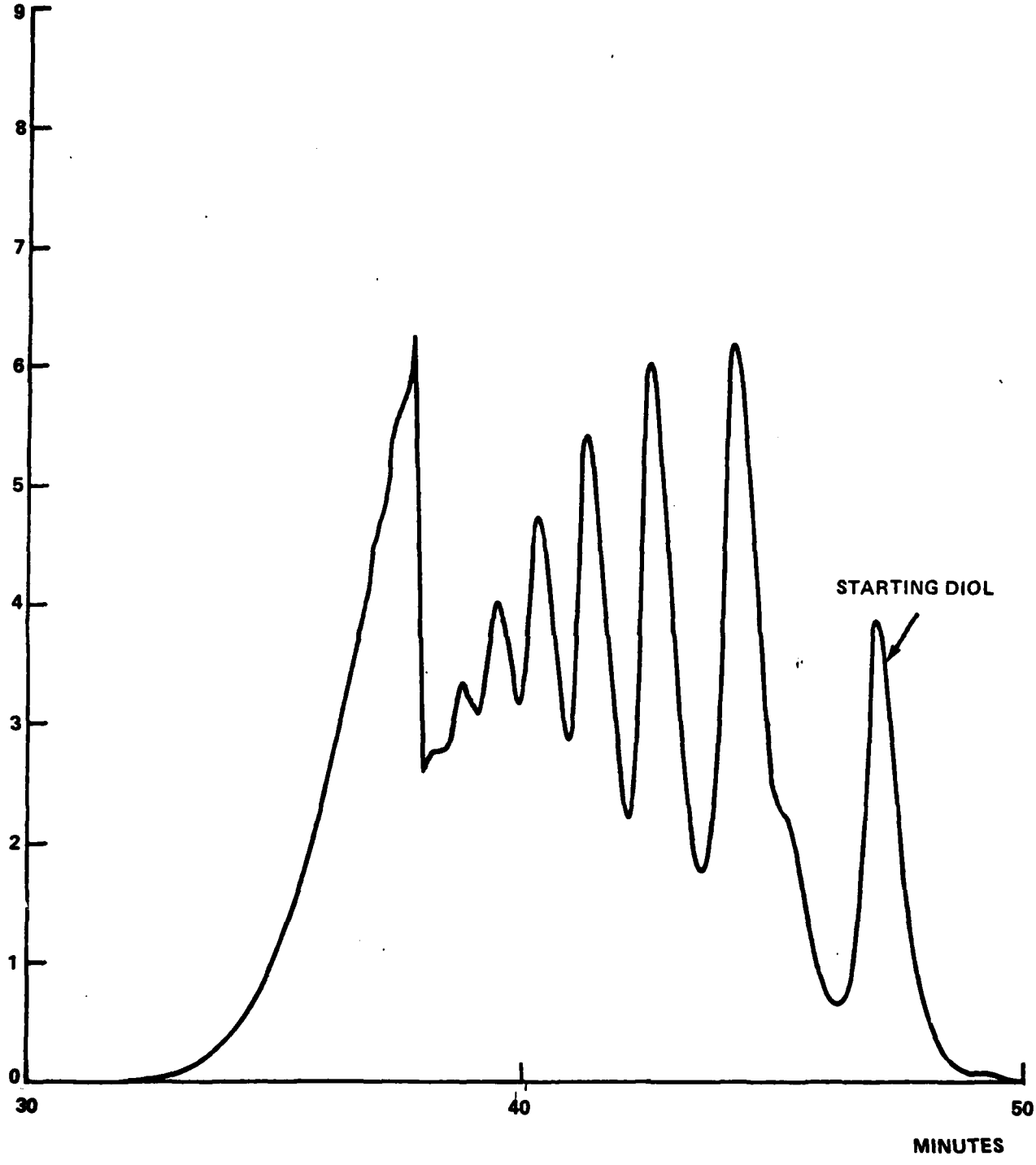


FIGURE 3. POLYFORMAL OF 2

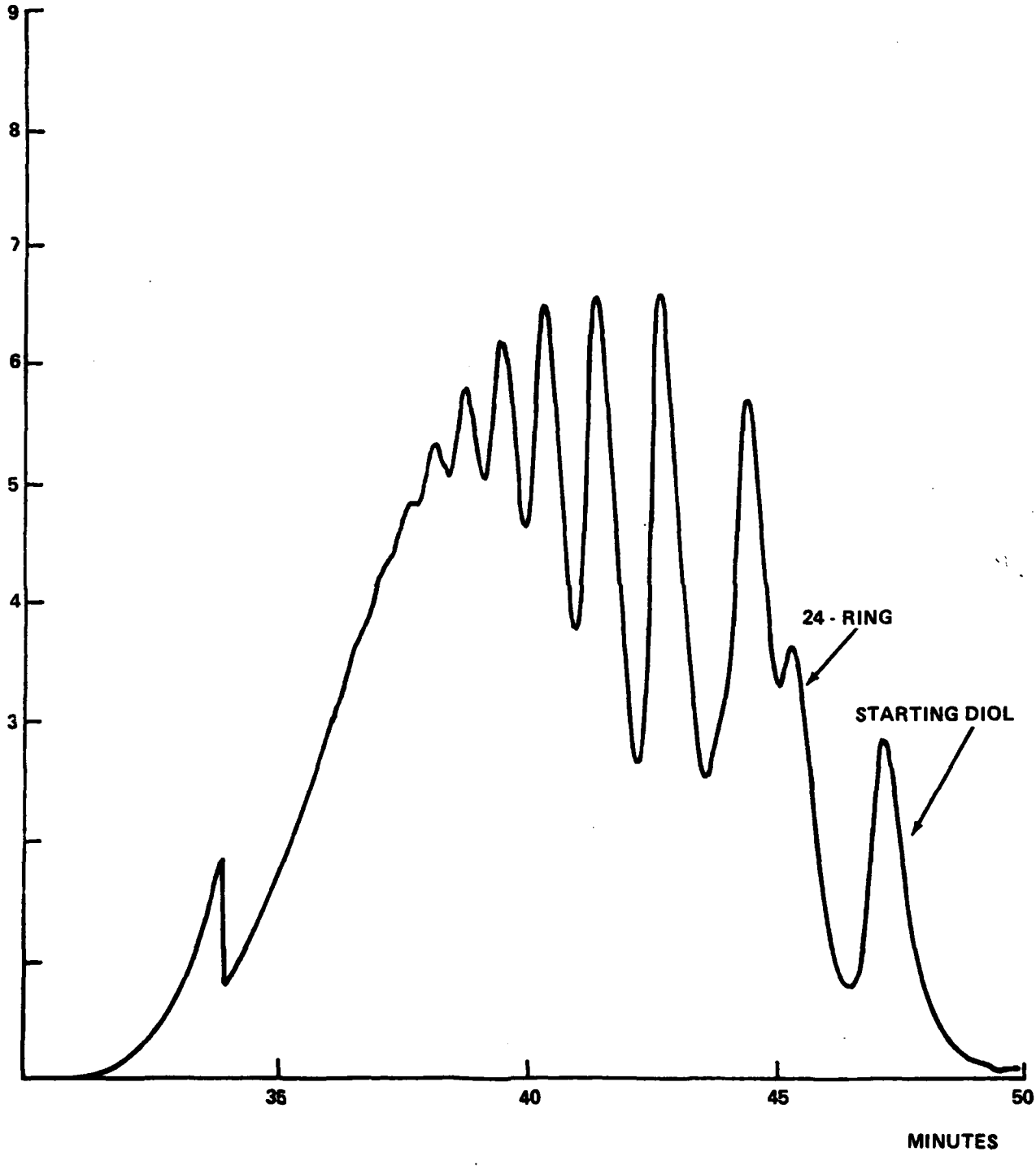


FIGURE 4. POLYFORMAL OF 2

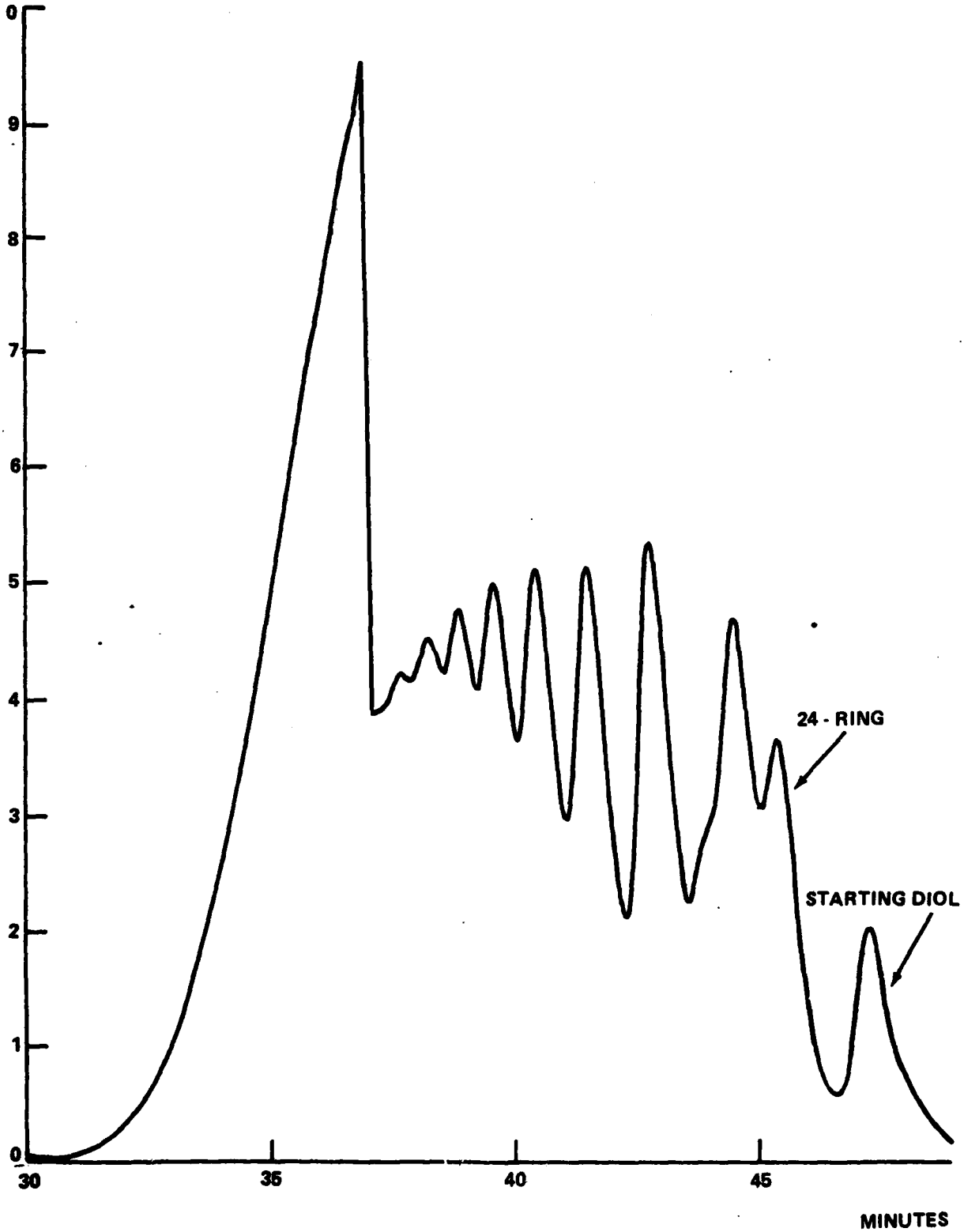


FIGURE 5. POLYFORMAL OF 2

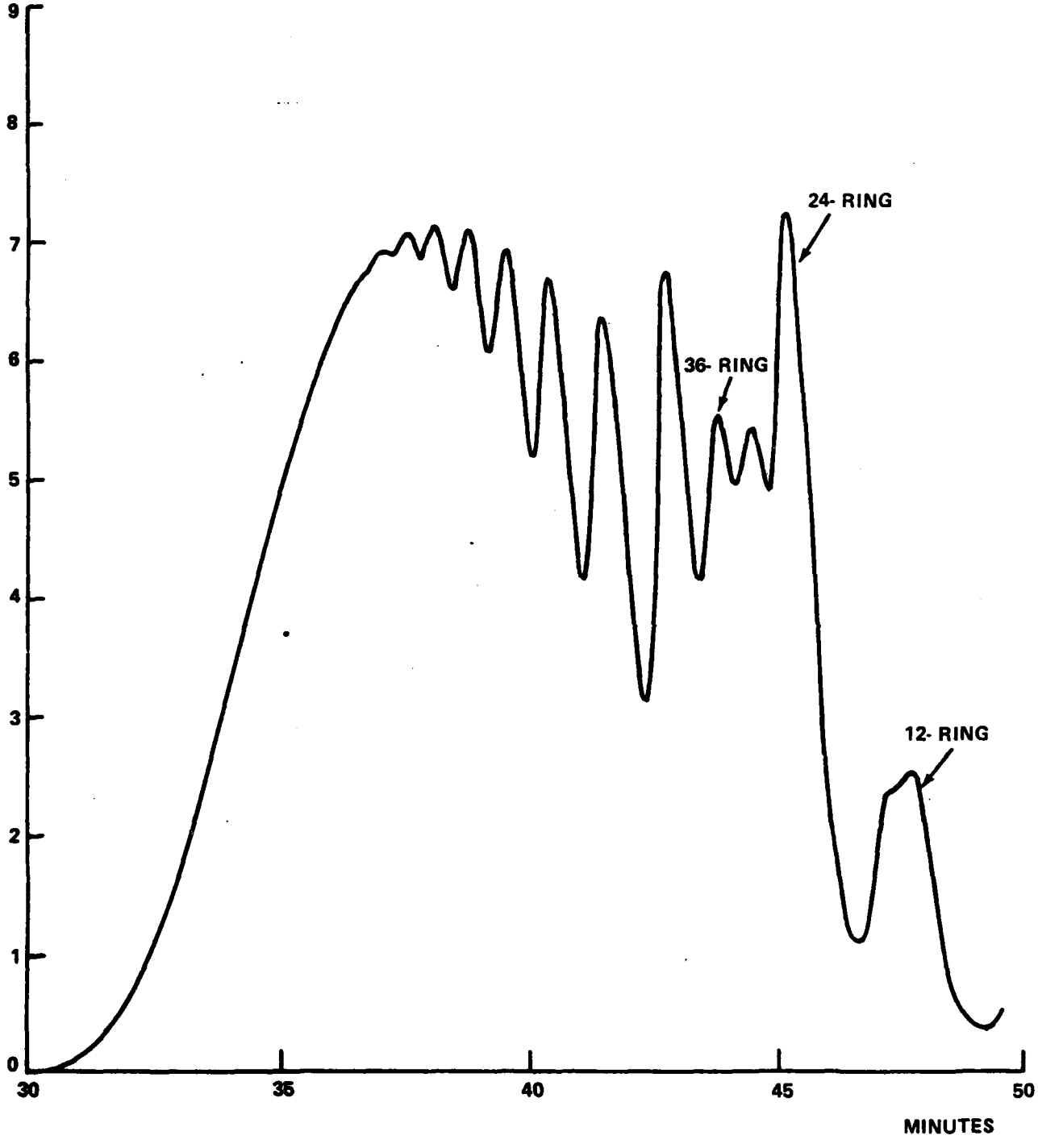


FIGURE 6. POLYFORMAL OF 2

Table 1. Solubility of Polyformal of 2 in Energetic Plasticizers

Plasticizer	Weight Ratio Plasticizer: Polymer	Solubility		
		25°C	50°C	75°C
BDNPF/A	1:1	PARTIAL	YES	YES
BDNPF/A	2:1	YES	-	YES
FEFO	1:1	YES	-	YES
FEFO	2:1	YES	-	YES

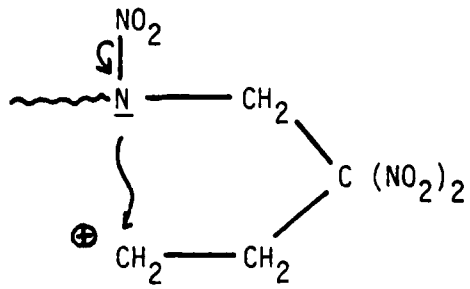
During work to determine suitable conditions for the preparation of 3,3-dinitrobutyl formal it was noted that the dinitrobutanol reacted with strong acids even in the absence of formaldehyde. It was found that this reaction led to the formation of the symmetrical ether and proceeded best with catalytic amounts of triflic acid under conditions of azeotropic removal of the water formed, (refluxing dichloroethane). A similar reaction was observed for 3,3,3-trinitropropanol but in lower yield and accompanied by extensive decomposition of the starting material. It was thought that this reaction might be useful for the preparation of polyethers

$$RC(NO_2)_2CH_2CH_2OH \xrightarrow[-H_2O]{CF_3SO_3H} RC(NO_2)_2CH_2CH_2OCH_2CH_2C(NO_2)_2R$$

R = Me : 80%

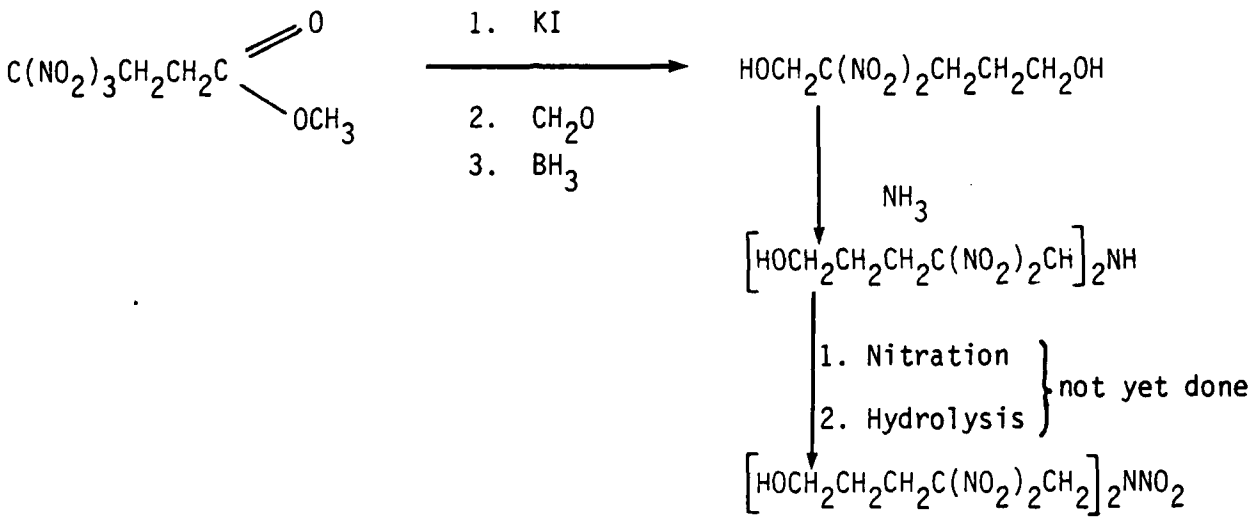
R = NO_2: 20%

from 2. However, when this reaction was applied to 2, decomposition with liberation of nitric oxides occurred, even when the solvent reflux temperature was lowered (CH_2Cl_2). A possible explanation for this facile loss of NO_2 would be denitration via the intermediate carbonium ion 3. Under less acidic conditions where a carbonium ion such as 3 is not formed, for example in refluxing CF_3COOH and CF_3COOH/H_2SO_4 mixtures, 2 is stable and unreactive. An alternative route to polyethers of 2 would be the preparation of the ditriflate of 2 and reaction of it with 2 in the presence of a base. This has not yet been investigated fully.



3

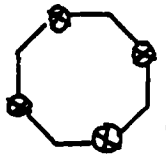
Work has also been started on the synthesis of 4, a homolog of 2. This would be an alternative diol for preparing polymers such as the formal, carbonate, or ether. These polymers would be somewhat less energetic but more easily prepared than those derived from 2.



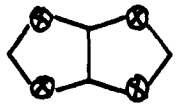
4

Potentially Dense Nitramines

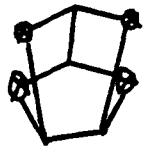
As outlined previously,[1] investigations into crystal density/molecular structure relationships have identified cyclic and polycyclic molecules of the type shown below as candidate high density compounds. The first set of density values shown are for the all-nitramines, where as the numbers in parentheses are for compounds in which half of the nitraza groups are replaced by gem-dinitro.[4] Note the trend to higher densities with increasing number of rings in the molecule, and the increasing density difference between all-nitramine and mixed nitraza/gem dinitro compounds.



(a)

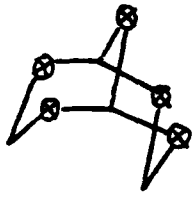


(b)

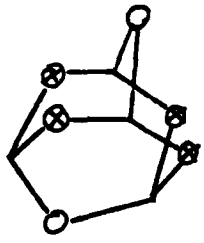


(c)

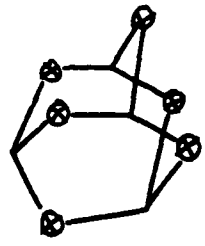
ρ_o = 1.79 (1.79) 1.91 (1.88) 2.05 (1.98) g/cm^3



(d)

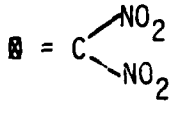


(e)



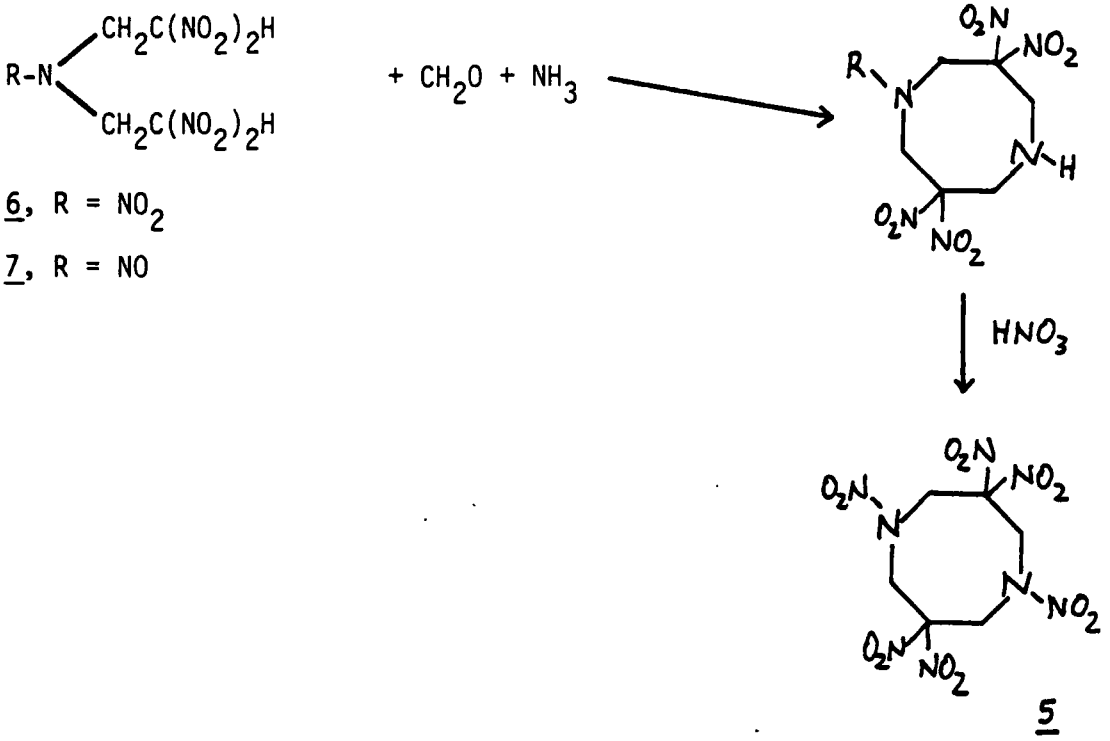
(f)

ρ_o = 1.97 (1.93) 2.08 (2.01) 2.11 (2.02) g/cm^3



AND/OR $N\text{-}NO_2$

Last year we reported the synthesis of 1,3,3,5,7,7-hexanitroperhydro-1,5-diazocine, 5, an example of structure (a) with mixed $N\text{-}NO_2$ and $C(NO_2)_2$ moieties. Some additional work was carried out on this and related compounds.[2] Contrary to our earlier as well as Russian observations, we now find that 5 can be prepared in 70 percent yield by condensation of bis(dinitroethyl)nitramine, 6, with CH_2O and NH_3, followed by nitration of the resulting amine. This is a considerable improvement over the earlier synthesis since the nitramine starting material is more readily prepared than the nitrosamine, 7, which was previously used. About 150g of 5 was prepared for a preliminary burning rate determination as well as study of its chemical transformation with bases (see below).

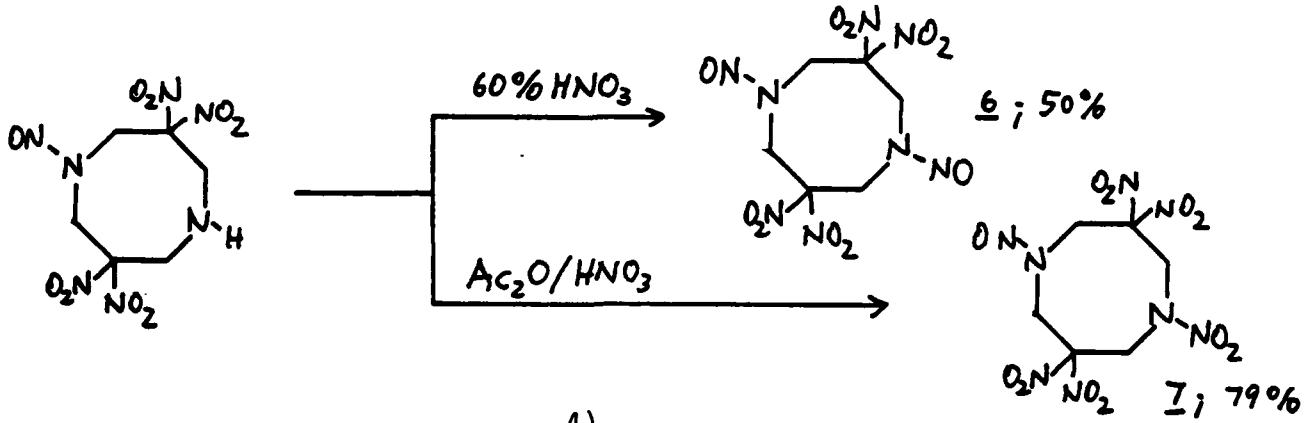


6, R = NO_2

7, R = NO

5

Two nitroso analogs of 5 were prepared from the appropriate intermediates of the 5 syntheses shown above.

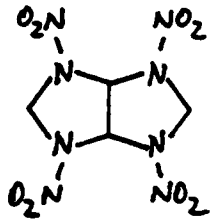


A monotonous decline in density[4] was observed when the nitro groups in 5 were successively replaced by nitroso:

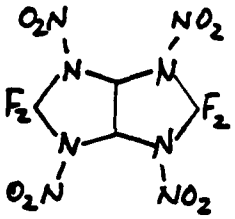
5 , ρo = 1.86 g/cm^3; 6, ρo = 1.82 g/cm^3; 7, ρo = 1.78 g/cm^3

A paper describing the work on the diazocines has been written and submitted for publication. A copy of the manuscript is shown in Appendix A. Experimental procedures described there are not repeated in the experimental section of this report.

A second significant effort during 1982 was directed towards the synthesis of bicyclic compounds of type (b), specifically bicyclo-HMX, 8, and 9 and 10.



8



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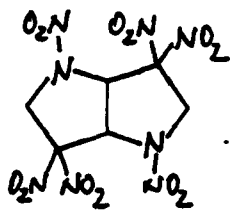
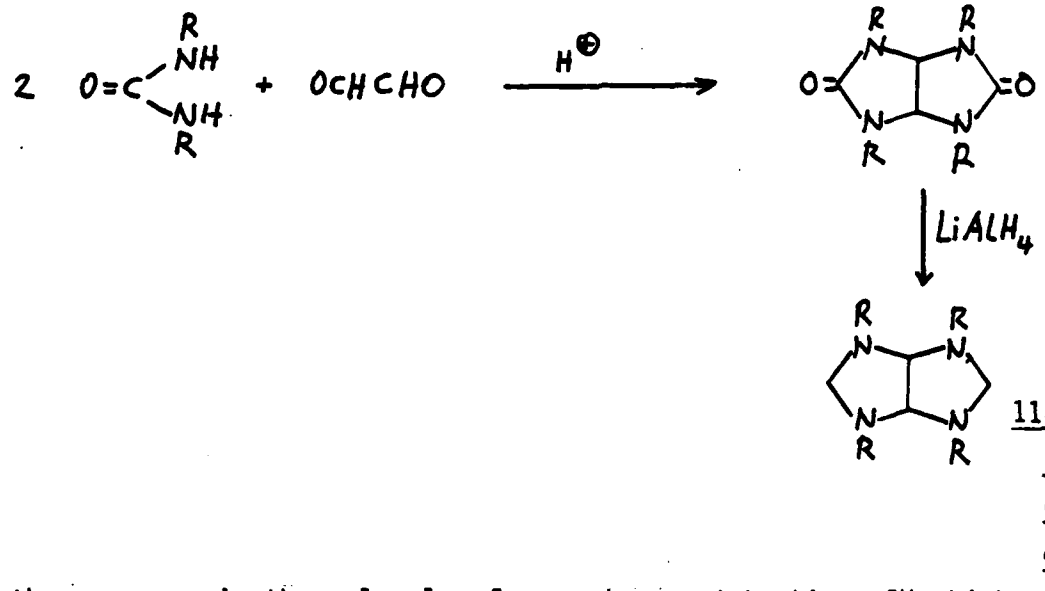


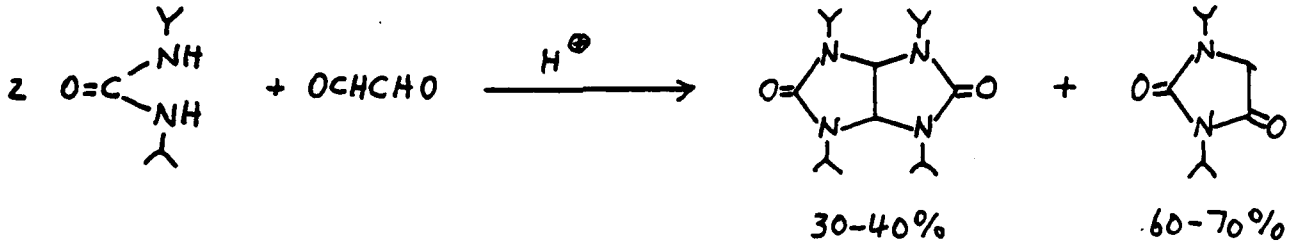
10

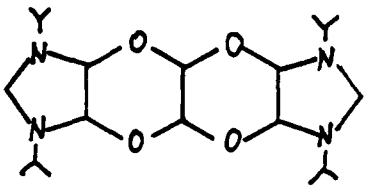
One approach involved the synthesis of tetraalkyl analogs of 8 which could be expected to undergo nitrolysis based upon results of our earlier work on this subject.[1] The synthesis of 11a by the method shown had been reported in the literature[6] but the prospects for its conversion to 8 were not good because of



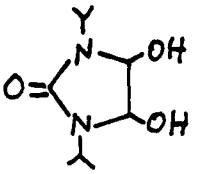
11a: R=CH_3
b: R=$C(CH_3)_3$
c: R=$CH(CH_3)_2$
d: R=$CH_2C_6H_5$

the presence in the molecule of secondary and tertiery CH which would be expected to react in preference to the CH_3 groups in any nitrolysis, nitrosolysis, or oxidation reaction needed for this purpose.[7] We felt that 11b would be a much more suitable intermediate and attempted its preparation using the reported procedure for 11a with N,N'-di-tert-butyl urea as starting material. This attempt as well as many others using various modifications of reaction conditions were unsuccessful. Under mild conditions, no reaction was observed between the urea and glyoxal; under more stringent conditions of acid catalysis, loss of tert-butyl occurred and a mixture of products was formed. Diisopropyl urea on the other hand reacted readily with aqueous glyoxal to give readily separable mixtures of tetraisopropylglycol uril and N,N'-diisopropyl hydantoin. Another compound isolated from this reaction under certain conditions has been identified tentatively as 12. The structure of a fourth product, 13, is uncertain (see experimental section). Attempts to isolate the intermediate 14 were not successful.





12



14

Y = $CH(CH_3)_2$

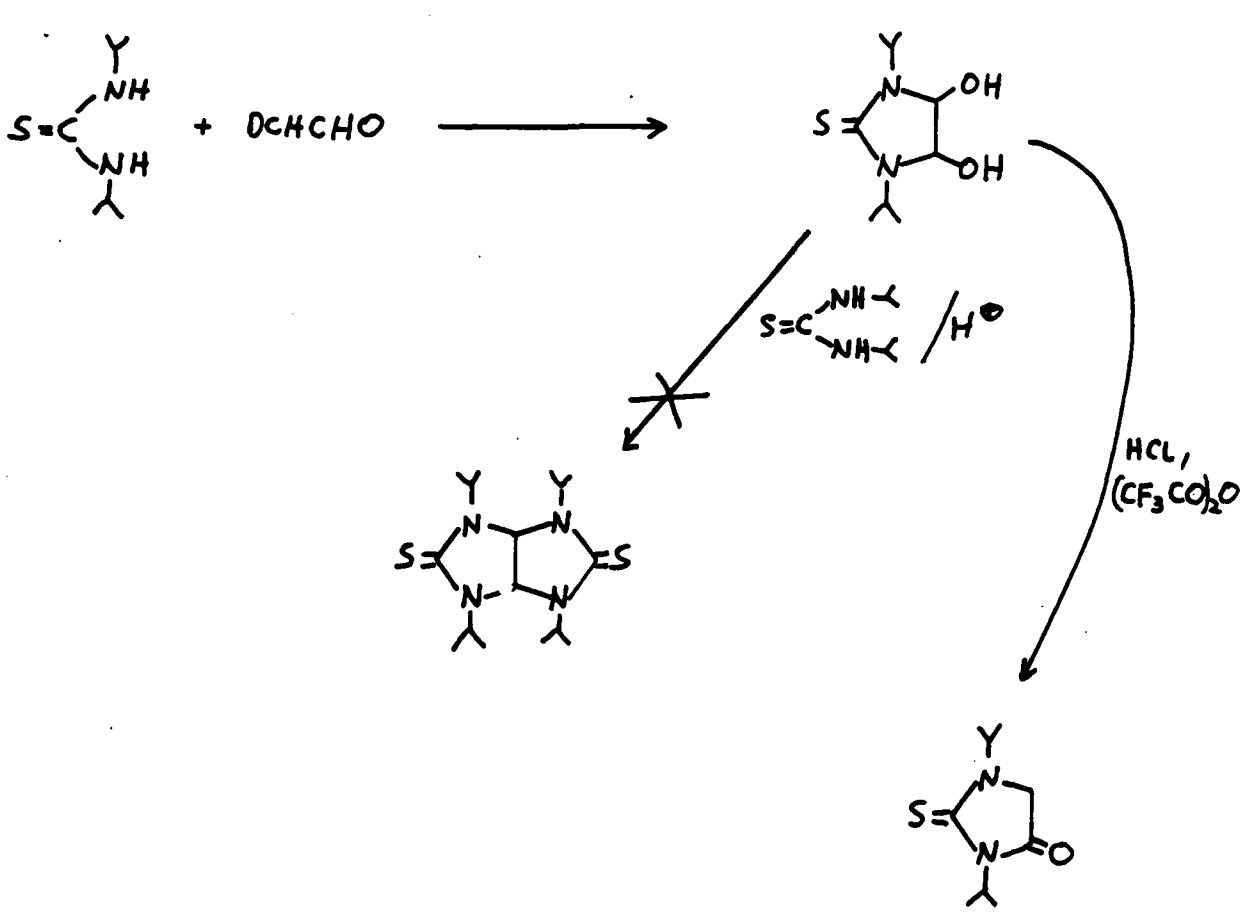
The reduction of tetraisopropylglycol uril gave 11c in about 70% yield.

The initial characterization of 11c revealed that it is not very stable. Storage at room temperature leads to decomposition within a few days. In the refrigerator in a closed container it has been stored unaffected for several weeks. The compound is extremely sensitive to acids. No picrate or hydrochloride could be prepared. Dichloromethane solutions decompose completely within 24 h, more rapidly in the presence of catalytic amounts of acetic acid. This is in contrast to 11a, which is stable under these conditions. It is believed that the unusual properties of 11c are caused by steric crowding due to the isopropyl groups which is relieved by ring opening. Indeed the NMR spectrum of 11c shows that rotation about the exocyclic C-N bonds is completely inhibited. Steric crowding is probably also responsible for the failure of tetra-tert-butylglycol uril formation as mentioned above.

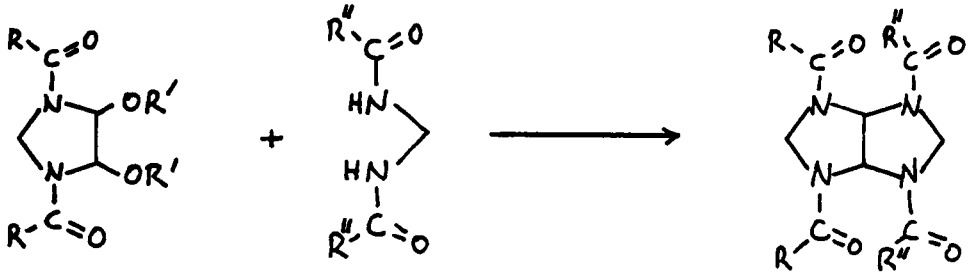
The sensitivity of 11c to acids and presumably other reagents which coordinate with nitrogen severely limits its usefulness as an intermediate for 8. However, oxidation under basic conditions may lead to removal of the isopropyl groups without destroying the ring system. This and similar approaches to the conversion of 11c to 8 will be considered in subsequent work.

Tetrabenzylglycol uril is of interest as an intermediate to 11d, which may be amenable to hydrogenolysis to the unsubstituted tetrazabicyclooctane. Unfortuanately our attempts to synthesize this glycol uril have so far been unsuccessful.

We have also investigated the preparation of thioglycol urils as possible intermediates to 9. It was found that diisopropyl thiourea reacted readily with glyoxal to form the mono adduct. However, further attempts at condensations leading to the glycol uril gave only the thiohydantoin. Apparently the dihydroxyimidazolidinethione rearranges to the hydantoin very easily in an acid medium.

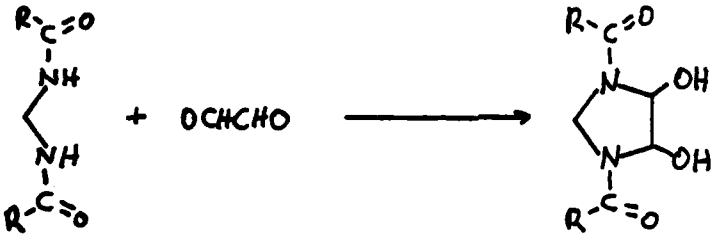


Another approach to the synthesis of the bicyclo-HMX system which we started work on is the condensation of methylene bisamides with their mono adducts to glyoxal, or derivatives of these. This approach leads to an intermediate for which



R, R', R'' = H, CH_3, CF_3 etc.

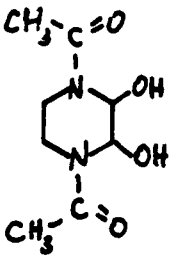
nitrolysis to 8 should be more straight forward than for 11c. On the other hand, previous workers have reported discouraging results with this approach because the initial condensation reaction could not be accomplished. We have so far only prepared a number of starting materials as shown in the equations below.



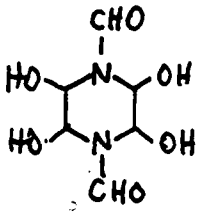
15a; R = H: trans only

15b; R = CH_3: mixture of cis-trans (about 1:1)

15b was acetylated with acetic anhydride to give the diacetate; the trifluoroacetates and triflates of 15a and 15b are currently being synthesized. Two other intermediates of interest are 16 and 17. 16 was prepared successfully by reaction of diacetylethylenediamine with aqueous glyoxal. Initial attempts to repeat the reported[87] preparation of 17 were not sucessful, but these efforts will be continued.

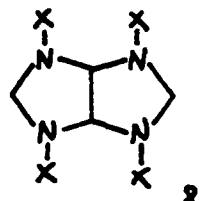


16



17

16 could condense with 15a or b to a bicyclo [4·3·0] nonane while 17 is a potential intermediate for some new target compounds shown below which appear to be more promising than bicyclo-HMX on the basis of their calculated densities and oxygen balance.



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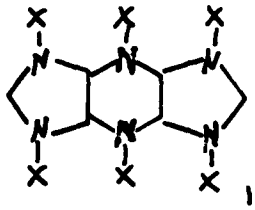
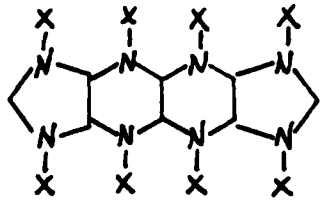


18



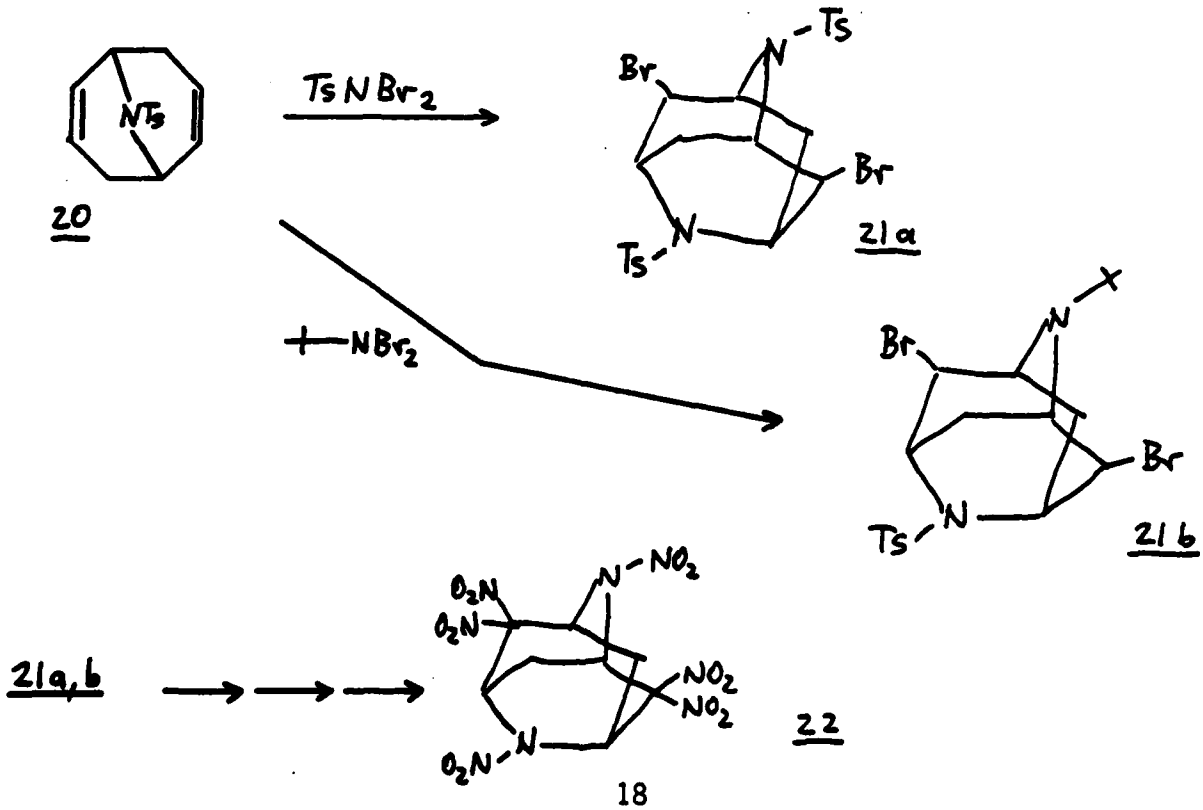
19

X = NO_2

ρo(calc'd):	1.91	1.95	1.96 g/cm^3
	$3H_2O/1CO_2/3CO$	$4H_2O/2CO_2/4CO$	$5H_2O/3CO_2/5CO$

Our efforts to synthesize 8, 18, and 19 are continuing.

The third effort initiated in 1982 under this task was to investigate approaches to compounds of type (d) - (f). We have synthesized the known[9] N-tosyl-9-azabicyclo [3·3·1] nonadiene, 20, and are working on its conversion to 21a and 21b.



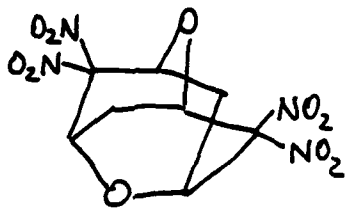
20

21a

21b

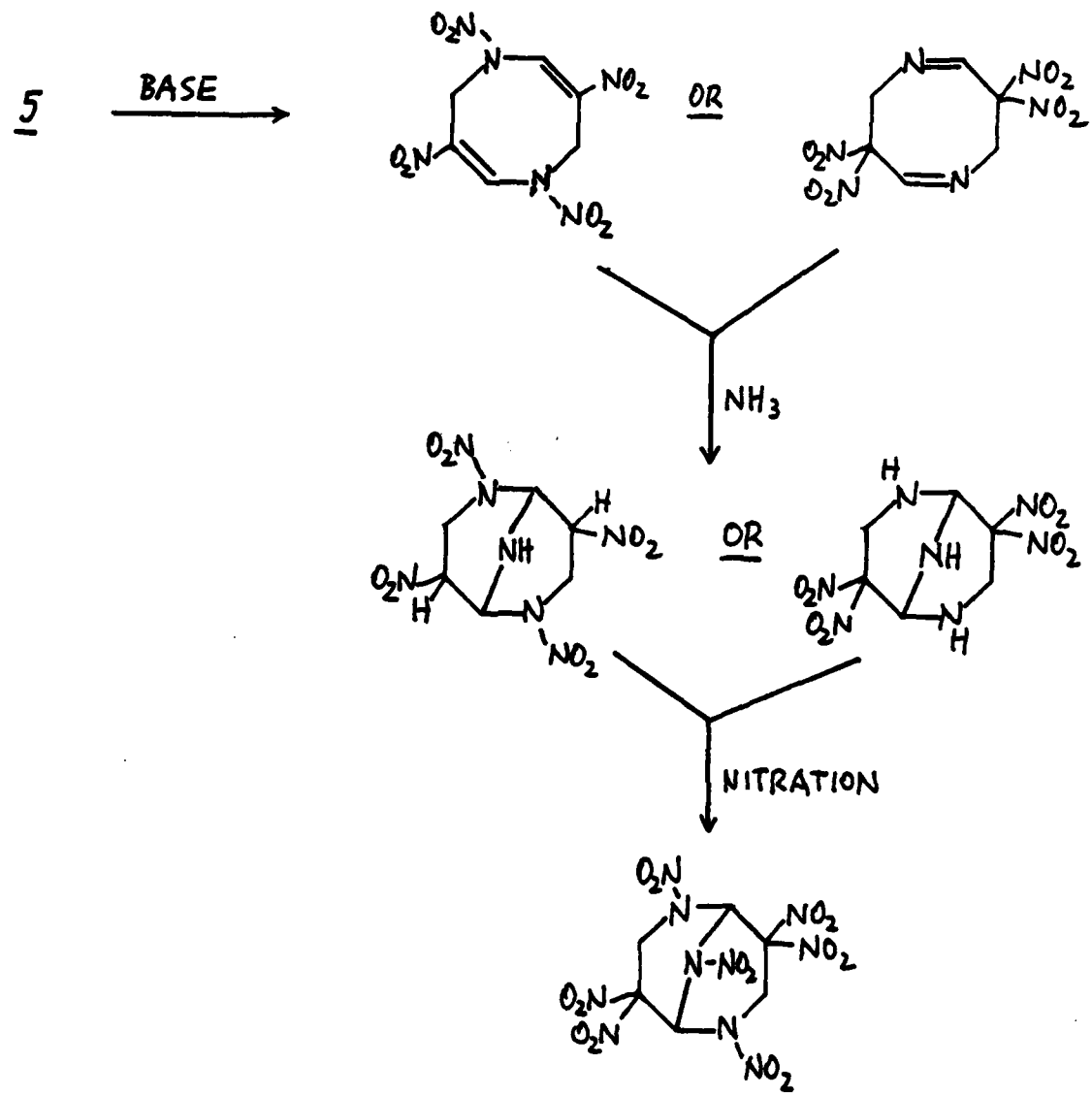
22

Also in progress is the synthesis of the dioxa analog 23. We are investigating the reaction of 5 with bases to generate another unsaturated intermediate for



23

the polyazabicyclononane and eventually polyazaadamantane systems, as shown in the scheme below.



Experimental Section

Melting points are uncorrected. Microanalyses are by Galbraith Laboratories, Knoxville, Tennessee. NMR spectra were obtained on a Varian EM-390 spectrometer. Chemical shifts are in ppm relative to TMS as internal standard. Temperatures are in ^{o}C unless noted otherwise.

1,10-Dichloro-4,4,7,7-tetranitro-2,9-dioxadecane. 8.8g of aluminum chloride was added rapidly to an ice-cooled slurry of 9.8g 1, 50 ml dry dichloromethane, and 2.0g trioxane under a dry nitrogen atmosphere. The mixture was stirred 2 days at room temperature, then it was poured over a mixture of 80g crushed ice and 1.5 ml conc. sulfuric acid, and the mixture stirred vigorously until all aluminum precipitates had dissolved. The product solution was separated, the aqueous phase extracted once with dichloromethane, and the combined organic phases washed rapidly with a near saturated, ice cold sodium bicarbonate solution. After drying ($MgSO_4$) the solvent was evaporated in vacuo to give 10.3g of an oil whose NMR spectrum was consistent with the title structure; ^{1}H NMR ($CDCl_3$): δ2.70 (s, 2H), 4.31 (s, 2H), 4.57 (s, 2H); the material was not purified or characterized further.

Preparation of 2,2,5,5-Tetranitrohexanediol Polyformal in Sulfolane/CF_3SO_3H. In a small 3-neck flask under a dry nitrogen atmosphere 1g of 1 was dissolved with stirring in 4 ml dry (sieves) sulfolane. 83 mg of trioxane was added, followed by 0.4 to 0.6 ml triflic acid. The mixture was stirred 24 h at ambient temperature, then poured over a mixture of ice and dil. H_2SO_4 with manual agitation. The insoluble product was allowed to settle, the aqueous phase was decanted and the residue triturated twice with water, allowing each time the product to settle completely before proceeding further. Finally the product was taken up in ethyl acetate, the solution dried ($MgSO_4$), filtered, and freed from solvent in vacuo to give the crude polymer. The product was characterized by GPC analysis as described below; see Fig. 1.

Separation of Cyclic Formals from 2,2,5,5-Tetranitrohexanediol Polyformals. The crude product described above was triturated overnight with 5 ml dichloromethane, the mixture filtered and the solid washed with dichloromethane/hexane (1:1) on the filter. This product weighed 610 mg and gave the GPC shown in Fig. 2.

GPC Analysis of Polyformals; General Procedure. Analyses were carried out with an instrument fitted with a Waters Model 6000 pump using a UV (254 nm) detector. The column was Varian Micropack TSK type 3000H, cross-linked polystyrene/divinylbenzene, particle size 8-10 μ; column length 80 cm, I.D. 7.5 mm. The sample (25-50 mg) was dissolved in 5 ml deaerated tetrahydrofuran and a 10 μl aliquot was injected with a U6K liquid chromatograph injector. The flowrate was generally 0.5 ml/min.

3,3-Dinitrobutanol. This compound was prepared from 4,4-dinitropentanoic acid via the acid chloride and azide and 3,3-dinitrobutyl isocyanate following the procedures of Gold and Eremenko.[10] None of the intermediates were purified. The crude product was purified by filtering a solution in dichloromethane through a column of silica gel and eluting with sufficient dichloromethane. The fractions which were pure by TLC were combined; pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 1H), 2.59 (s, 3H), 3.18 (, 2H), 4.25 (t, 2H). This compound was characterized further by conversion into the formal and ether (see below).

3,3-Dinitrobutyl Formal. A mixture of 1.18g 3,3-dinitrobutanol, 5 ml dry (sieves) sulfolane, 0.1g trioxane, and 0.5 ml BF_3 etherate was stirred at ambient temperature for 24 h and then poured into dil. $NaHCO_3$ solution. The product was extracted with dichloromethane, the solution washed 3 times with water, dried ($MgSO_4$), and freed from solvent to give 1.17g (92%) crude dinitrobutyl formal. ^1H NMR ($CDCl_3$): δ 2.19 (s, 6H), 2.87 (t, 4H), 3.72 (t, 4H), 4.53 (s, 2H).

3,3,3-Trinitropropyl Formal. 1.4g of crude 3,3,3-trinitropropanol, 5 ml nitromethane, 0.108g trioxane, and 0.5 ml BF_3 etherate were stirred under nitrogen at ambient temperature for 20 h. TLC analysis of an aliquot showed considerable unreacted trinitropropanol present. Another 0.5 ml BF_3 etherate was added and the mixture stirred another 20 h. TLC analysis indicated no further reaction had occured. The mixture was diluted with a small quantity of dichloromethane and filtered through a 15 cm long column (2 cm diameter) of silica gel. Elution with dichloromethane gave several fractions of fairly pure formal followed by the unreacted trinitropropanol. The formal fractions were combined, filtered and freed from solvent to give 0.8g of an oil which did not crystallize. ^1H NMR ($CDCl_3$): δ 3.36 (t, 4H), 3.95 (t, 4H), 4.58 (s, 2H).

Preparation of Polyformals of Nitrazadiol 2; General Procedure. Under an atmosphere of dry N_2, 1g of 2 was dissolved in 3 ml of acetonitrile or sulfolane and 0.72 to 0.82g trioxane was added. The solution was cooled in an ice bath and 0.42 to 0.75 ml BF_3 etherate was added with stirring. Stirring was continued for 24 h at room temperature; then the mixture was poured into a solution of 0.75g to 1.0g $NaHCO_3$ in 80 - 100 ml water. The product was allowed to settle and the aqueous phase was decanted. The product was triturated with water and allowed to settle again. The water was decanted, the polymer was dissolved in ethyl acetate, the solution dried ($MgSO_4$) and freed of solvent in vacuo to give the crude polymer.

3,3-Dinitrobutyl Ether. A mixture of 0.75g 3,3-dinitrobutanol, 15 ml 1,2-dichloroethane, and 0.1 ml triflic acid was refluxed through a reverse Dean-Stark trap for 20 h and allowed to cool. The solution was washed with water, dried ($MgSO_4$), filtered and freed of solvent to give an oil which soon solidified. TLC and NMR analyses showed the presence of small amounts of starting material and dinitrobutyl triflate (see below) in addition to the title compound as major component. Recrystallization from dichloromethane/hexane gave the pure ether, mp 66-7°. ^1H NMR ($CDCl_3$): δ 2.13 (s, 6H), 2.80 (t, 4H), 3.58 (t, 4H).

Anal. calc'd for $C_8H_{14}N_4O_9$: C, 30.97; H, 4.55; N, 18.06. Found: C, 31.14; H, 4.56; N, 17.86.

3,3-Dinitrobutyl Triflate. Under a dry N_2 atmosphere and with ice cooling and stirring, a mixture of 1.42g 3,3-dinitrobutanol, 0.77g pyridine, and 3-4 ml dichloromethane was added in 30 min. to a solution of 1.65 ml triflic anhydride in 10 ml dichloromethane. The mixture was stirred 1 h at ice bath temperature and poured on top of a short column of silica gel wetted with dichloromethane. The organic material was eluted with 2 x 100 ml dichloromethane. The first 100 ml fraction contained the pure triflate, the 2nd 100 ml contained a small amount of triflate, some starting alcohol, and an unidentified by-product. Removal of the solvent from the first fraction gave an oil which decomposed at room temperature but could be stored for some time in the refrigerator. ^1H NMR ($CDCl_3$): δ 2.23 (s, 3H), 3.07 (t, 2H), 4.72 (t, 2H).

2,2-Dinitropentanediol-1,5. A mixture of 30.6g methyl trinitrobutyrate, 48g KI, and 290 ml methanol was stirred at room temperature 2.5 - 3 days and filtered; the yellow salt was washed with cold methanol and air dried. A suspension of the crude salt in 120 ml 70% aqueous THF was cooled to 15° and 10.8g 36% formalin was added with stirring. 10.2g conc. HCl (37%) was added until pH paper indicated 3.0 in the lower aqueous layer. The mixture was stirred at room temperature for 3 h, acidified, diluted with an equal volume of water and extracted with CH_2Cl_2 (3 x 50 ml). The combined extracts were washed with 100 ml of water (acidified), dried (Na_2SO_4), filtered, and freed of solvent to give 20.9g (73%) liquid product which was identical by IR and NMR with an authentic sample of methyl 5-hydroxy-4,4-dinitropentanoate prepared by the method of Klager.[11]

A solution of 14.7g methyl 4,4-dinitro-5-hydroxypentanoate in an equal volume of THF was added in a steady stream to a THF solution of BH_3 · THF (109 ml, 0.97M, 0.106 mols) under nitrogen. After the reaction was refluxed for 1.5 h, 15.0 ml of conc. HCL was added dropwise over an hour period, during which time H_2 gas evolved. The mixture was stirred an additional 30 min, and 70 ml of H_2O and 50 ml of toluene were added. The organic layer was collected, dried over Na_2SO_4, filtered and stored at 8°C overnight. The precipitate of boric acid was filtered off and the filtrate stripped of solvents in vacuo leaving an oily residue which was chromatographed on an 7 x 1 inch dry packed silica gel column. Elution with an initial solvent system of toluene was followed by 6% ethyl acetate/toluene and finally 10% ethyl acetate/toluene. The fractions shown by TLC to contain the pure diol product were conbined and evaporated to give 7.4g of the diol in 54% yield. ^{1}H NMR (D_2O): δ (2.14 (m, 2H), 3.20 (t, 2H), 4.16 (t, 2H), 5.03 (s, 2H).

Tetraisopropylglycol uril and N,N'-Diisopropyl hydantoin. A mixture of 2.88g diisopropyl urea, 1.45g 40% aqueous glyoxal, 9 ml water and 2 ml conc. HCl was stirred at room temperature for 1 week and filtered. The solid was allowed to air dry and weighed 1.8g. Filtering a methylene chloride solution of the crude product through a column of silica gel removed some unreacted starting material and gave the pure glycol uril; mp (isopropyl ether) 150°. ^{1}H NMR (CD_2Cl_2): δ 1.26, 1.35 (dd, 24H), 3.63 (h, 4H), 5.01 (s, 2H).

Anal. calc'd for $C_{16}H_{30}N_4O_2$: C, 61.90; H, 9.74; N, 18.03. Found: C, 62.10; H, 9.80; N, 18.13.

Evaporation to dryness at room temperature of the filtrate from the glycol uril gave crude diisopropyl hydantoin which was similarly purified by filtration through silica gel. ^{1}H NMR ($CDCl_2$): δ 1.18 (d, 6H), 1.40 (d, 6H), 3.74 (s, 2H), 4.34 (m, 2H).

On one occasion this preparation was carried out at slightly elevated temperature and with 2.5 - 3 ml conc. HCl. The crude solid which was filtered off contained an additional product (13) which eluted first from the silica column. The structure of this product has not been elucidated at this point. ^{1}H NMR ($CDCl_3$): δ 1.21 (d, 12H), 1.42 (d, 6H), 3.97 (m, 2H), 4.77 (h, 1H), 6.64 (broad, 2H); no change on shaking with D_2O.

When the reaction between diisopropyl urea and aqueous glyoxal on the above scale was carried out in the presence of only 2-3 drops of conc. HCl, still another product was obtained in place of the glycol uril. The NMR spectrum

indicates that the structure may be that of 12. The material was not further characterized. ^{1}H NMR (CD_2Cl_2): δ 1.27 (d, 12H), 4.12 (h, 2H), 4.98 (s, 2H), 5.70 (s, 4H).

2,4,6,8-Tetraisopropyl-2,4,6,8-tetrazabicyclo [3·3·0] octane. A mixture of 7g tetraisopropylglycol uril, 300 ml dioxane, and 8.5 $LiAlH_4$ (under N_2) was heated at 90° for 24 h. After cooling, 35 ml ethyl acetate was added dropwise with stirring and ice-cooling and the mixture stirred for several h. The mixture was filtered with suction and the filter cake washed with ether. The filtrate was concentrated in vacuo to give 4.9g of product which was pure by NMR. ^{1}H NMR (CD_2Cl_2): δ 0.93-1.07 (dd, 24H), 2.96 (h, 4H), 3.30 (d, 2H), 3.62 (d, 2H), 4.40 (s, 2H).

4,5-Dihydroxy-1,3-diisopropylimidazolidine-2-thione. A mixture of 1.6g diisopropyl thiourea, 5g 40% aqueous glyoxal, 10 ml water, and 3 drops conc. HCl was stirred at room temperature for several days. Filter, air dry. ^{1}H NMR (acetone-d_6 + 1 dr. D_2O): δ 1.28 (dd, 12H), 4.47 (h, 2H), 5.09 (s, 2H).

Attempted Reactions of Dihydroxy-N,N'-diisopropylimidazolidinethione in Presence of Acids; N,N'-diisopropyl-2-thiohydantoin. A mixture of 0.20g of the imidazolidine thione, 0.14g N,N'-diacetyl-1,2-diaminoethane, 4 ml water, and 1 ml conc. HCl was stirred 24 h at room temperature; work-up gave the thiohydantoin as the only new product. The same result was obtained in the absence of the diacetylethylenediamine. Reaction of 0.22g imidazolidine thione in 3 ml dichloromethane with 0.42g (282.5 µl) trifluoroacetic anhydride at room temperature overnight also gave the thiohydantoin as the only product. ^{1}H NMR (CD_2Cl_2): δ 1.25 (d, 6H), 1.45 (d, 6H), 3.85 (s, 2H), 5.04 (m, 2H).

1,3-Diacetyl-4,5-diacetoxyimidazolidine. A mixture of 1,3-diacetyl-4,5-dihydroxyimidazolidine (9.14g, 50 mmol) and acetic anhydride (100 ml) was heated at reflux for 1 hour. The excess anhydride and acetic acid was then evaporated under vacuum and the solid residue was triturated with ether (50 ml) and filtered to yield 1,3-diacetyl-4,5-diacetoxyimidazolidine (9.70g, 71.3%); mp 138-151°C. Recrystallization of a sample from benzene gave colorless needles; mp 128-150°C. The ^{1}H NMR spectrum ($CDCl_3$) showed a mixture of cis and trans isomers in about equal proportions. Methyl multiplets were centered at δ 2.10 and singlets at 5.02 (trans-CH_2) and 6.35 (trans-CHs). An AB quartet was centered at 5.05 (cis-CH_2) and a doublet at 6.45 (cis-CHs).

Anal. calc'd for $C_{11}H_{16}N_2O_6$: C, 48.52; H, 5.92; N, 10.29. Found: C, 48.58; H, 6.02; N, 10.34.

1,4-Diacetyl-2,3-dihydroxy-1,4-diazine. A mixture of 1.44g N,N'-diacetyl-1,2-diaminoethane, 1.45g 40% aqueous glyoxal, and 5 ml water was stirred for 24 h, then allowed to eveporate to dryness. The residue was pure title compound by NMR analysis. ^{1}H NMR (D_2O): δ 2.48 (s, 6H), 3.82 (s, 4H), 5.35 (s, 2H).

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2. M. B. Frankel, E. R. Wilson, E. F. Witucki, Rocketdyne Final Report for Contract N60921-81-C-0285, 25 Feb 1983. The procedure for preparation of 1 described in this report is given in Appendix B.

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5. The crystal density of 5 was determined from the cell dimensions by H. Ammon of the University of Maryland, those of 6 and 7 by R. Gilardi, Naval Research Laboratory, Washington, D.C.

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11. K. Klager, J. Org. Chem. 16, 161 (1951).

APPENDIX A - MANUSCRIPT SUBMITTED FOR PUBLICATION

SYNTHESIS OF POLYNITRO- AND NITRONITROSOPERHYDRODIAZOCINES

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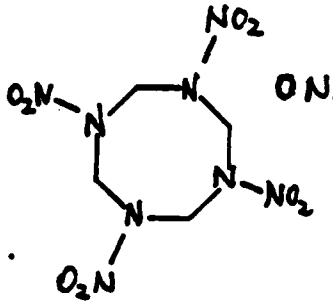
HMX, 1, is one of the most important ingredients of military high energy propellants and explosives whose properties have been investigated extensively.[1] To aid in the interpretation of the observed behavior, especially in thermal decomposition and burning, structural analogs are needed for comparison. We report here the synthesis of a number of polynitroperhydro-1,5-diazocines (2a, b; 3a) which serve this purpose.



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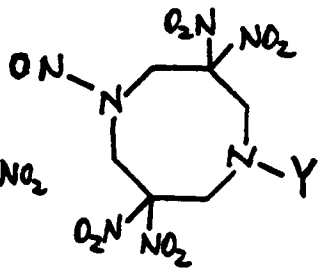
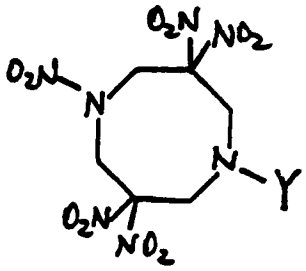


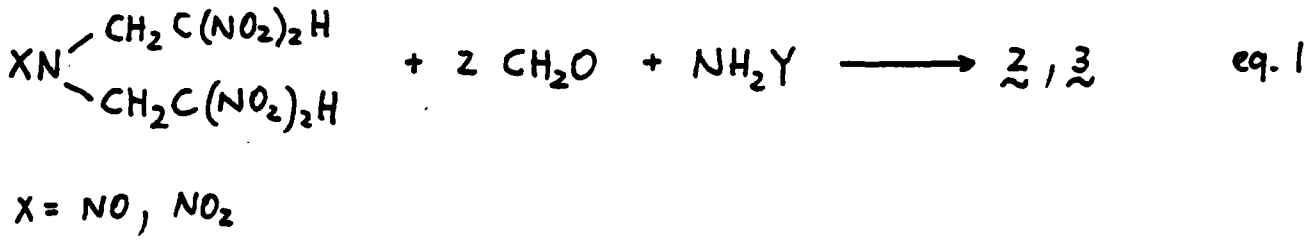
2a: Y = NO
2b: Y = NO_2
2c: Y = Me
2d: Y = tert-butyl
2e: Y = i-propyl
2f: Y = H



3a: Y = NO_2
3b: Y = Me
3c: Y = CHO
3d: Y = i-propyl
3e: Y = H

Compounds 2a, b and 3a are readily recognized as potential products of a multiple Mannich condensation between dinitromethane, formaldehyde, and a

nitrogen species which can subsequently be converted to N-NO or $N\text{-}NO_2$. However, attempts at direct condensation of these reagents gave only the previously reported 2,2-dinitroethylamine zwitterion[2] or 6-membered ring compounds.[3] A more promising approach appeared to be the use of a preformed bis(2,2-dinitroethyl)amine derivative as a substrate for the Mannich condensation in which case the formation of the above alternative products is prevented (eq 1). This sequence has recently been applied sucessfully[4] to the synthesis of



eq. 1

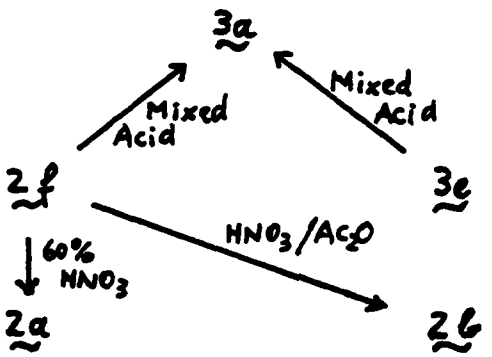
$X = NO, NO_2$

2c ($X = NO$, $Y = CH_3$). Our attempts to convert that compound to 2a, b, or 3a were, however, not sucessful. While nitrolysis with mixed acid gave 3b in 39% yield, further treatment of 3b or treatment of 2c with other nitrolyzing or nitrosolyzing agents (nitric acid (100%)/ammonium nitrate, nitric acid/acetic anhydride/hydrochloric acid, and sodium nitrite/acetic acid) resulted either in decomposition of the substrate or in no reaction. The methyl group in 3b was readily oxidized to formyl (3c, 80% yield) but nitrolysis of the latter with nitric acid/acetic anhydride was also not successful.

In view of the ease with which the N-tert-butyl group is nitrolyzed in bis(2,2-dinitroethyl)amines[3] the synthesis of 2d was attempted (eq. 1, X = NO, Y = tert-butyl). However, under a variety of conditions, no 2d was formed. With isopropylamine, on the other hand, 2e was obtained in 47% yield illustrating an apparent importance of steric effects in the formation of the N-alkyl derivatives of 2. Contrary to previous experience with other types of isopropylamines,[5] 2e could again not be nitrolyzed to 2b or 3a. Mixed acid treatment led only to replacement of the nitroso group to give 3d (93%) while other reagents (nitric acid or nitric acid/ammonium nitrate)

with either 2e or 3d led to destruction of the substrate. It was possible, however, to remove the isopropyl group oxidatively (CrO_3/HOAc) in 2e and 3d to give the parent amines 2f and 3e, respectively.

The direct synthesis of 2f and 3e according to eq 1 (Y = H) was attempted and was successful in the case of 2f in 81% yield and (with X = NO_2) in the case of 3e in a surprisingly good yield despite the reported failure of the reaction with X = NO_2 and Y = Me.[4,6] With 2f and 3e now readily accessible, the synthesis of 2a and b and 3a was accomplished by routine nitration, nitrosation and/or nitrolysis of these amines as shown in scheme 1.



Scheme 1. Nitration and Nitrosation of 2f, 3e

Attempts to convert 2b to 3a with mixed acid or 90% nitric acid were unexpectedly unsuccessful (recovery of starting material). This indicates that in the conversion of 2f to 3a nitrolysis of N-NO precedes nitration of N-H.

The 'H-N.M.R spectrum of 2a in acetone solution indicates the presence of the cis and trans isomers. Two sets of 2 singlets are observed in the ratio of about 3:2. This is analogous to the situation reported[7] for 1,4-dinitrosopiperazine which also appears as a mixture of cis (40%) and trans (60%) isomers in the N.M.R spectrum. The existance of isomers is confirmed by the ^{13}C-N.M.R spectrum of 2a which shows 2 sets of 2 singlets in a ratio of about 3:2 for the CH_2 groups, and 3 singlets for the $C(NO_2)_2$ groups. Two of the latter singlets can be attributed to the cis isomer and one (of higher intensity) to the trans isomer where the two $C(NO_2)_2$ groups are equivalent.

Independant confirmation of the structures of 2a, b, and 3a comes from the total crystal structures recently determined by H. Ammon and R. Gilardi.[8] In contrast to the N.M.R results in solution, the crystallographic data indicate that 2a exists only in the trans configuration in the solid state.

Experimental Section; CAUTION: Several of the compounds reported herein are sensitive explosives and should be handled with appropriate care. Melting points are uncorrected. Elemental analyses (Table 1.) were obtained commercially. ^{1}H-N.M.R spectra are from various sources, ^{13}C-N.M.R spectra were recorded on a Varian XL-200 spectrometer; chemical shifts are given in parts per million from Me_4Si.

Bis(2,2-dinitroethyl)nitramine:

Dry bis(potassium-2,2-dinitroethyl)amine (22.88g) was added to methylene chloride (114 mL) and the mixture cooled in an ice-salt bath at -10 to -20°C. To this mixture was added dropwise at 0°C a mixture of nitric acid (90%, 20.6 mL) and conc. sulfuric acid (4.4 mL) over ½ h followed by conc. sulfuric acid (91.5 mL) over 1 h. After the mixture was stirred 2 h. at 0°, the solid was filtered off, washed with 30 mL each of cold 80%, 60%, 30%, 10% and 1% sulfuric acid and 30 mL ice water and air dried to give 14.0g white solid.

The methylene chloride was allowed to evaporate from the filtrate after which the solution was cooled and filtered to remove the solid. The solid was washed with 20 mL each 10% and 1% sulfuric acid and ice water to give 1.37g after air drying for a total of 15.37g bis(2,2-dinitroethyl)nitramine (71%). The material was identical by N.M.R. with an authentic sample [9,10] and was generally recrystalized from methylene chloride before use.

Mannich Condensations; General Procedure:

To the bis(2,2-dinitroethyl)nitroso(or nitro)amine was added aqueous methanol and acetic acid followed, with ice cooling, by the aqueous amine and aqueous formaldehyde (37%). The pH was then adjusted to the desired value

with acetic acid or ammonia after which the mixture was stirred at the specified conditions. The solid was then filtered off, washed with water and dried in vacuo.

3,3,7,7-Tetranitro-1-nitroso-5-isopropyl-perhydro-1,5-diazocine (2e):

The condensation was done with bis(2,2-dinitroethyl)nitrosoamine (0.5g), 60% methanol (4.5 mL), 0.23g acetic acid, 20% isopropyl amine (1.1mL) and 0.6 mL formaldehyde at pH 3.5-4.0. The reaction was heated at 30°C for 3 h, the solid isolated and the filtrate (excluding the wash water) heated at 30°C overnight to give a total of 0.29g (47%) of 2e; m.p. (from methylene chloride/hexane) 123-124°C.

'H-N.M.R. (deuteriochloroform): δ 0.90 (d, 6H), 2.70 (m, 1H), 3.43 (s, 2H), 3.83 (s,2H), 5.00 (s, 2H), 5.58 (s, 2H).

3,3,7,7-Tetranitro-1-nitroso-perhydro-1,5-diazocine (2f):

A mixture of bis(2,2-dinitroethyl)nitrosoamine (14.0g), 60% methanol (126 mL), 6.4g acetic acid, ammonia (12.9 mL, (29%) in 13 mL water) and 16.8 mL formaldehyde at pH 4 was stirred at room temperature overnight to give 2f; yield: 13.8g (81%); m.p. (from methylene cholride/hexane) 148°C onset of decomposition, 159.5-160.5°C melts with decomposition.

'H-N.M.R. (deuteriochloroform/acetone d_6): δ = 3.0-3.3 (1H), 3.60 (d, 2H), 4.0 (d, 2H), 4.97 (s, 2H), 5.83 (s, 2H).

1,3,3,7,7-Pentanitro-perhydro-1,5-diazocine (3e):

A mixture of bis(2,2-dinitroethyl)nitramine (13.2g), 40% methanol (93 mL), 4.3 mL acetic acid, ammonia (9.7 mL (29%) in 9.7 mL water) and 12.3 mL formaldehyde at pH 4.8-5.0 was stirred at room temperature 1.5 h to give 3e; yield: 12.7g (85%); a small amount of impurity present can be removed by dissolving the product in acetone, filtering off the impurity and removing the solvent. Its m.p. and 'H-N.M.R. spectrum agreed with those of 3e prepared by the chromium trioxide oxidation of 3d (see below).

1-Methyl-3,3,5,7,7-pentanitro-perhydro-1,5-diazocine (3b):

A mixture of bis(2,2-dinitroethyl)nitramine (0.10g), 60% methanol (1.3 mL), 0.04 mL acetic acid, 25% methyl amine (0.9 mL) and 0.12 mL formaldehyde at pH 4 was stirred at room temperature 1 h to give 3b; yield: 0.19g (15%). Its m.p. and 'H-N.M.R. spectrum agreed with those of 3b prepared by the nitrolysis of 2c (see below).

Chromium Trioxide Oxidations; General Procedure:

To glacial acetic acid was added chromium trioxide and the substrate. After stirring at room temperature for the specified time, the product was isolated by pouring the mixture onto ice, filtering off the solid, washing it with water and drying it in vacuo.

Oxidation of 1-Methyl-3,3,5,7,7-pentanitro-perhydro-1,5-diazocine (3b → 3c):

3b (0.1g) was reacted with 0.2g chromium trioxide in 2.5 mL acetic acid overnight to give a beige solid (0.083g, 80%) which was purified by passing it through a short column of silica gel eluting with methylene chloride/acetonitrile; m.p. 169°C onset of decomposition, 231.5-232.5°C melts.

'H-N.M.R. (acetone d_6): δ = 5.00 (s, 2H). 5.27 (s, 2H), 5.38 (s, 2H), 5.69 (s, 2H), 8.38 (s, 1H).

Oxidation of 3,3,7,7-Tetranitro-1-nitroso-5-isopropyl-perhydro-1,5-diazocine (2e → 2f):

2e (0.078g) was reacted with 0.21g chromium trioxide and 2.5 mL acetic acid for 2.5 h to give 0.046g crude product. The 'H-N.M.R. spectrum is indicative of a mixture of 3,3,7,7-tetranitro-1-nitroso-perhydro-1,5-diazocine (2f) (see above) and a small amount of starting material.

Oxidation of 3,3,5,7,7-Pentanitro-1-isopropyl-perhydro-1,5-diazocine (3d → 3e):

3d (0.098g) was reacted with 0.21g chromium trioxide and 2.5 mL acetic acid for 1 h to give 0.083g crude solid (94%) which was purified by passing it through a short column of silica gel; m.p. 160°C onset of decomposition, 173.5-174.5°C melts with decomposition.

^{1}H-N.M.R. (acetone d_6): δ = 3.33 (m, 1H), 4.20 (d, 4H), 5.50 (s, 4H).

Mixed Acid Nitrations; General Procedure:

To concentrated sulfuric acid cooled in an ice bath was added the substrate followed by a mixture of nitric acid and sulfuric acid. After stirring for the specified time, the product was isolated by pouring the mixture onto ice, filtering off the solid, washing it with water and drying it in vacuo.

Nitrolysis of 3,3,7,7-Tetranitro-1-nitroso-5-isopropyl-perhydro-1,5-diazocine (2e → 3d):

2e (0.109g) was nitrolyzed with 3.4 mL sulfuric acid and a mixture of 0.8 mL 90% nitric acid and 1.4 $mL_{\Lambda}^{conc.}$ sulfuric acid for 1 3/4 h in an ice bath to give 3,3,5,7,7-pentanitro-1-isopropyl-perhydro-1,5-diazocine (3d); yield: 0.10g (93%); m.p. (from methylene chloride/hexane): 129-130°C.

^{1}H-N.M.R. (deuteriochloroform): δ = 0.89 (d, 6H), 2.64 (m, 1H), 3.81 (s, 4H), 5.29 (s, 4H).

Nitration/Nitrolysis of 3,3,7,7-Tetranitro-1-nitroso-perhydro-1,5-diazocine (2f → 3a):

2f (0.075g) was reacted with 3.4 $mL_{\Lambda}^{conc.}$ sulfuric acid and a mixture of 0.8 mL 90% nitric acid and 1.4 $mL_{\Lambda}^{conc.}$ sulfuric acid for 15 min in an ice bath to give 1,3,3,5,7,7-hexanitro-perhydro-1,5-diazocine 3a; yield: 0.08g (90%). The product was recrystalized from acetonitrile or nitromethane; m.p. 250°C (decomposition).

^{1}H-N.M.R. (acetone d_6): δ = 5.70 (s); ^{13}C-N.M.R. (acetone d_6) δ = 56.0 (s), 117.0 (s).

Nitration of 3,3,5,7,7-Pentanitro-perhydro-1,5-diazocine (3e → 3a):

3e (0.75g) was nitrated with 3 $mL_{\Lambda}^{conc.}$ sulfuric acid and a mixture of 1 mL 99% nitric acid and 1.5 $mL_{\Lambda}^{conc.}$ sulfuric acid for 45 min in an ice bath and 10 min at room temperature to give 1,3,3,5,7,7-hexanitro-perhydro-1,5-diazocine (3a); yield: 0.83g (99%). Its m.p. and ^{1}H-N.M.R. spectrum agreed with those of 3a prepared by the nitration/nitrolysis of 2f (see above).

Nitrolysis of 1-Methyl-3,3,7,7-tetranitro-5-nitroso-perhydro-1,5-diazocine (2c → 3b):

2c (1.0g) was nitrolyzed with 10 mL conc. sulfuric acid and a mixture of 2.4 mL 90% nitric acid and 4.2 mL conc. sulfuric acid for 15 min in an ice bath to give 1-methyl-3,3,5,7,7-pentanitro-perhydro-1,5-diazocine (3b); yield: 0.405g (39%); m.p. (from methylene chloride/hexane): 147°C onset of decomposition, 163.5-164.5°C melts.

'H-N.M.R. (acetone d_6): δ = 2.42 (s, 3H), 4.23 (s, 4H), 5.52 (s, 4H).

3,3,5,7,7-Pentanitro-1-nitroso-perhydro-1,5-diazocine (2f → 2b):

To acetic anhydride (5 mL) at 0-5°C was added oxide free nitric acid (90%, 1.5 mL) followed by 2f (0.2g). The mixture was stirred at 0-5°C for 10 min, poured onto ice and the resulting mixture stirred 1 h at room temperature. The solid was filtered off, washed with water and dried in vacuo. Recrystalization from nitromethane gave 2b; yield: 0.22g (79%); m.p. 229°C (decomposition).

'H-N.M.R. (acetone d_6): δ = 5.32, 5.37 (2s, 4H), 5.73 (s, 2H), 6.20 (s, 2H); ^{13}C-N.M.R. (acetone d_6): = δ 51.8 (s). 57.2 (s), 57.4 (s), 116.5 (br s), 118.8 (br s).

3,3,7,7-Tetranitro-1,5-dinitroso-perhydro-1,5-diazocine (2f → 2a):

To nitric acid (60%, 7.0 mL) at 40-45°C was added 2f (0.2g). The mixture was heated at 40-45°C for 5 min and then was poured onto ice. The solid was filtered off, washed with water and dried in vacuo to give 0.109g which was recrystalized from nitromethane to remove a small amount of starting material; m.p. 190°C onset of decomposition, 228-229°C melts.

'H-N.M.R. (acetone d_6): δ = 4.81 (s), 5.26 (s), 5.73 (s), 6.16 (s); ^{13}C-N.M.R. (acetone d_6): δ = 48.7 (s), 49.1 (s), 55.5 (s), 55.9 (s), 113.3 (s), 115.9 (s), 118 (s).

Table 1. Microanalyses

Compound	Fomula	Calculated	Found
3a	$C_6H_8N_8O_{12}$	C 18.75 H 2.08 N 29.17	C 19.04 H 2.07 N 28.96
2b	$C_6H_8N_8O_{11}$	C 19.57 H 2.19 N 30.44	C 19.42 H 2.29 N 30.13
2a	$C_6H_8N_8O_{10}$	C 20.46 H 2.29 N 31.82	C 20.45 H 2.35 N 31.62
3b	$C_7H_{11}N_7O_{10}$	C 23.80 H 3.14 N 27.16	C 24.00 H 3.20 N 27.54
3c	$C_7H_9N_7O_{11}$	C 22.90 H 2.47 N 26.70	C 22.77 H 2.64 N 26.76
2e	$C_9H_{15}N_7O_9$	C 29.60 H 4.14 N 26.84	C 29.80 H 4.28 N 26.71
3d	$C_9H_{15}N_7O_{10}$	C 28.35 H 3.97 N 25.72	C 28.17 H 3.79 N 25.42
2f	$C_6H_9N_7O_9$	C 22.30 H 2.81 N 30.34	C 22.66 H 2.85 N 30.54
3e	$C_7H_9N_7O_{11}$	C 21.25 H 2.68 N 28.91	C 21.36 H 2.70 N 28.77

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APPENDIX B - PREPARATION OF 2,2,5,5-TETRANITROHEXANEDIOL-1,5
REPRODUCED FROM REF. 2

EXPERIMENTAL

GENERAL

Most of the products and starting materials are explosives of moderate to considerable sensitivity to initiation by impact, shock, friction, and other means and should be handled with care.

Melting points are uncorrected. Microanalyses are by Galbraith Laboratories, Knoxville, TN. Isolation and purification in many instances were accomplished by liquid chromatography for safety reasons. Infrared analyses were carried out with a Perkin-Elmer 137 infrared spectrophotometer. Gas-chromatographic analyses were carried out with an F&M 700 instrument using a 10 ft x 3/16 in stainless-steel column packed with 3% QF-1 on 40/80 mesh Chromosorb T. HPLC analyses were determined with a Waters HPLC unit.

1,4-Dinitrobutane (5)

This procedure is typical of the four runs that were made. To a mixture of 304.2 g (4.4 mol) of urea, 304.2 g (5.07 mol) of sodium nitrite and 2535 ml of DMF, cooled to 0 C, was added 219 g (1.014 mol) of 1,4-dibromobutane. The reaction mixture was stirred at 0 C for 2 hr.; at this point it had become a clear pale yellow solution. Phloroglucinol (269.4 g, 2.14 mol) was added portion-wise and then with the wet ice bath in place, the reaction mixture was allowed, with stirring, to warm to ambient temperature overnight. An equal quantity of methylene chloride was added and the

total solution was washed six times with water to remove DMF. Analysis by GC indicated the solution was completely free of DMF at this point. The methylene chloride was removed in vacuo yielding 67 g (45%) of crude 1,4-dinitrobutane. Pure 1,4-dinitrobutane, 40 g (27%) m.p. 33-34 C, was obtained by recrystallization from methanol, cooled to -78 C prior to filtration.

2,2,5,5-Tetranitro-1,6-hexanediol (2)

A total of 5 runs were carried out and the following represents a typical run. 1,4-Dinitrobutane (193 g, 1.3 mol) was added to a solution of sodium hydroxide (107.5 g, 2.6 mol, 98% assay) in 685 ml of water and the mixture stirred for 2 hours at 0 C. Formalin (211.5 g, 2.6 mol) was added all at once causing the temperature to rise to 15 C. After stirring the solution at 0-5 for 2 hours, sodium nitrite (185.4 g, 2.69 mol) was added; then a solution of 911.1 g (5.36 mol) of silver nitrate in 1050 ml of water was added all at once and the mixture stirred vigorously at 0 C for 1 hour. The precipitate was collected, dried in vacuo, and extracted with ether. Concentration of the ether extracts gave 170.5 g (44%) of a white solid, m.p. 116-122 C. Recrystallization from water containing a drop of 37% hydrochloric acid gave 103 g (26.6%) of product, m.p. 128-130 C.

1,4-Dibromo-1,4-dinitrobutane (10)

To 100 ml of methanol was added portion-wise 11.3 g (0.49 mol) of sodium at 0 C. A solution of 31.3 g (0.21 mol) of 1,4-dinitrobutane in 500 ml of methylene chloride was added dropwise in 30 minutes. The pale yellow slurry was stirred for an additional 30 min. at 0 C and a solution of 74 g (0.46 mol) of bromine in 90 ml of chloroform added in 45 min. at 0 C. The mixture was stirred for an additional hour at 0 C, filtered, and concen-

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